In the following examples the substrates will be human dentin, human enamel, and single-crystal fluorapatite surfaces. The polymerizing monomer and polymer will be that of methyl methacrylate. This resin was selected as an example because it is a typical, commonly used resin for the direct filling of dental cavities. Ordinarily the methyl methacrylate monomer contains about 0.5 percent N,N-dimethyl-p-toluidene reducing agent (accelerator for the peroxide decomposition) and the polymer powder contains 0.5 to 0.75 percent benzoyl peroxide initiator. Once the polymer and substrate have been determined, the surface-active comonomer is determined by the above operational definitions. In the case of the present example, the selection of the appropriate polar group, which would make the molecule surface-active for this given substrate, was determined by trial and error with various surface-active agents and powdered substrates in the surface-activity test described above. By this test method, the polar groups, making this type of molecule surface-active for this particular substrate, had an increasing order of effectiveness as follows: hydroxyl, amino, carboxyl, and groups theoretically capable of forming a five-atom amphoteric chelate ring with calcium. The affinity of this surface for water would be placed between that for hydroxyl and amino groups. For the present example the polymerizable group of the surface-active comonomer was a methacrylate group, making the surface-active comonomer capable of polymerizing (or copolymerizing) with the resin system.

In the present examples, such a surface-active comonomer, when diluted in an appropriate solvent and applied to a dentin, enamel or fluorapatite substrate prior to an application of a polymerizing resin system, results in a significantly more stable and stronger bond than when the surface-active comonomer was not used, other things being the same. Thus, in the present examples, the surface-active comonomer is applied in the manner of a primer, but its effectiveness should be also obtained by its being admixed with the monomer of the polymerizing system.

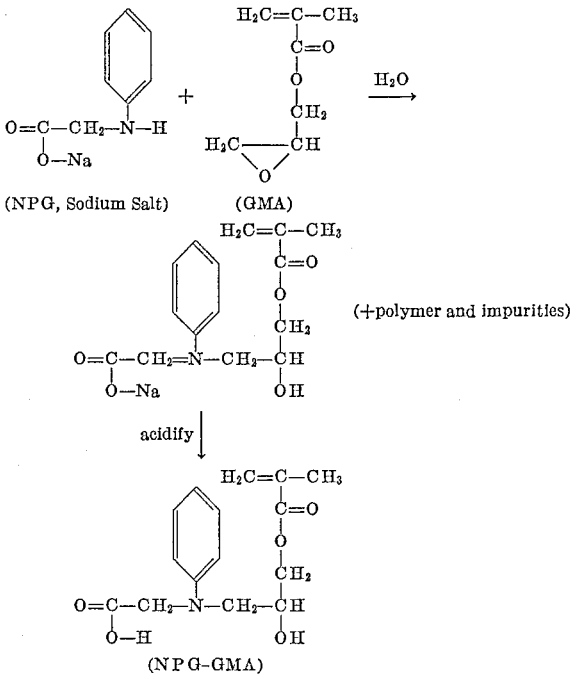
METHODS OF PREPARATION OF A SURFACE-ACTIVE COMONOMER

One example of a surface-active comonomer will be described here, although there are conceptually a large number of surface-active comonomers with subtile distinctions which would be suitable for a selected polymer and substrate.

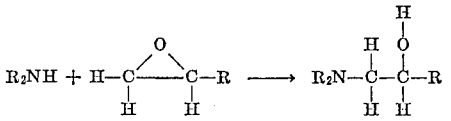
In accordance with one embodiment of the present invention the reaction product of N-phenyl glycine and glycidyl methacrylate, hereinafter abbreviated NPG–GMA, will be described and will serve as an example of a surface-active comonomer for hard tooth tissues and for a methacrylate resin system. The synthesis follows:

Four grams (0.01 mol) of NaOH, were dissolved in 100 milliliters of distilled water. To this was added 15.1 grams (0.1 mol) of N-phenyl glycine (Eastman #393). The solution was filtered on adding to a 300-milliliter reaction flask. This three-neck flask was equipped with dropping funnel, reflux condenser, and stirrer. To this solution 13.1 milliliters (14.2 grams or 0.1 mol) of glycidyl methcrylate (du Pont CP105; the 2,3-epoxy propyl ester of methacrylic acid) was added over five minutes with continuous stirring. Stirring was continued and the temperature rose from 23° C. to 30° C. in 2.5 hours, while a precipitate formed. To this, 400 milliliters of distilled water was added; the pH of the supernatant fluid was 6. The pH was brought up to 8 by the addition of NaOH. The reaction mixture was extracted three times with 100-milliliter portions of diethyl ether. The pH was then adjusted to 4 with HCl and $NaHCO_3$, yielding a light brown precipitate. The suspension was filtered and the solid product was stored at 5° C. in the dark until used. This crude product will be referred to as NPG–GMA (the addition reaction product of N-phenyl glycine and glycidyl methacrylate); it appeared to contain polymer and other impurities.

Portions of NPG–GMA were reciprocated from hot 1:1 methyl alcohol-water solutions and filtered. This appeared to give a mixture of product and polymer. The complex infrared spectrograph of the product, when compared with those of the intermediates was in agreement with the reactions and structures shown below:



The spontaneous addition reaction of secondary basic amines with oxirane groups:



is well known.

When N-phenyl glycine without added base was combined with glycidyl methacrylate (in benzene or 95 percent ethanol), heating was required to yield a reaction; and the product was soluble in acetone but was insoluble in aqueous NaOH, suggesting esterification of the carboxyl group.

The NPG–GMA was not appreciably soluble in water at pH 4 but was soluble in dilute aqueous NaOH, chloroform, methanol and ethanol.

When benzoyl peroxide was added to a methanol solution of NPG–GMA, a precipitate formed (overnight) which was insoluble in methanol and had a melting point above 250° C.

The NPG–GMA compound may be viewed as a polymerizable zwitterion in a hydrated environment; and its surface activity may be, at least in part, due to dipole association augmented by coordinate links of various types. The side chains of dentinal collagen contain anionic, cationic, and hydroxyl groups, and the surface of hydroxyapatite is believed to have localized electrostatic fields radiating out of the mineral surface. However, present theory and scale models suggest that NPG–GMA may be capable of tridentate cholation, satisfying one-half of the valency and three of the six to nine coordination numbers (positions) ascribed to calcium.

The present invention does not require a complete understanding of the mechanism, but only requires that the surface-active comonomer, which is the adhesion promoting agent, be surface-active to the substrate and at the same time be able to copolymerize with the ad-